STUDIES ON THE SHRINKAGE PHENOMENON: IX EFFECT OF PRETANNING PROCESSES ON APPARENT VOLUME SHRINKAGE AND RECOVERY

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Effect of pretanning (viz., soaking, liming, deliming and pickling) chemical treatments on the apparent volume shrinkage and recovery properties of goat skins is studied. No change in the apparent volume due to shrinkage or recovery of raw, limed and delimed samples was observed. Pickling brings about considerable apparent volume shrinkage irrespective of the shrinkage of the samples in water or pickle medium. The apparent volume shrinkage is little less in the case of samples shrunk in pickle medium.

The phenomenon of shrinkage behaviour of hide, skin, and leather with respect to shrinkage temperature, area, real volume and apparent volume has been studied by many workers earlier.[1-5] In these investigations, the study was confined to acetone dehydrated pelt or leathers. The change brought about in the dimensions was found to be characteristic of the tannage.[6] No work was done on the effect of the pretanning operations on the hydrothermal shrinkage. A systematic study on the effect of each pretanning operation on the area and apparent volume shrinkage and recovery after shrinkage of goat skins has been carried out. The results pertaining to changes in area due to shrinkage and recovery of samples at the end of various chemical treatments of beamhouse operations have been published.[7] The effect of various chemical treatments during beamhouse processing on the apparent volume shrinkage and recovery properties of skins is presented here.

Experimental

The procedure adopted by Ramanathan *et al*[6] which involves the use of Edwards Densimeter[8] was followed to find out the ratio of initial and final volume of skin/leather sample shrunk. Recently, the use of 'Varsol', a hydro-carbon, instead of mercury was recommended[9] for measuring apparent volume by the buoyancy method. But use of 'Varsol' involves degreasing of the samples and preimpregnation with it in the case of skin or leather and may not be suitable later for measuring the apparent volume change of the wet samples since hydrocarbons stick to the sample. Hence an Edwards Densimeter with mercury as the medium for displacement was used in the present work.

The relation between apparent volume before and after shrinkage is given by the formula:

$$\frac{\text{App. vol. before shrinkage } (v_1)}{\text{App. vol. after shrinkage } (v_2)} = \frac{(w_2 - w_1 + w)_1}{(w_2 - w_1 + w)_2}$$

where w is the weight of specimen, w_1 is the weight on the pan to sink the grip and w_2 is the weight on the pan to sink the grip and the specimen to the same extent.

Hence % app. vol. shrinkage =

$$\frac{(w_2 - w_1 + w)_1 - (w_2 - w_1 + w)_2}{(w_2 - w_1 + w)_1} \times 100$$

$$= \frac{(w_2 + w)_1 - (w_2 + w)_2}{(w_2 - w_1 + w)_1} \times 100 \text{ since } w_1 \text{ is constant.}$$

If v_3 is apparent volume after shrinkage,

% app. vol. recovery =

$$\frac{v_3 - v_2}{v_1 - v_2} \times 100$$

$$= \frac{(w_2 - w_1 + w)_3 - (w_2 - w_1 + w)_2}{(w_2 - w_1 + w)_1 - (w_2 - w_1 + w)_2} \times 100$$

$$= \frac{(w_2 + w)_3 - (w_2 + w)_2}{(w_2 + w)_1 - (w_2 + w)_2}.$$

Skins were processed as in previous studies on the effect of pretanning process on area shrinkage and recovery.[7]

Samples ($5 \times 1{\cdot}3$ cm.) were cut out at the end of each chemical treatment, dried and conditioned at $80 \pm 4°F$ and $65 \pm 2\%$ R.H. The pattern of cutting out samples in order to eliminate the locational variation is the same as that followed in area shrinkage studies of pretanning process.[7, 10] The dried samples were weighed in air and then in mercury. These samples were soaked in water for 2 hours and suspended in a perforated metal cage immersed in the heating medium (water), while one sample was clamped in a Theis shrinkage meter under tension.[11] As soon as the sample under tension exhibited shrinkage which was indicated on the dial, the perforated metal cage was taken out. It may be noted that there was a difference of about 4°C between the T_s of the sample under tension and the samples shrunk free by suspending in the medium. Shrunken samples were dried, conditioned and weighed in mercury. To know the extent of recovery, samples were again soaked in water overnight, dried, conditioned and weighed in mercury.

As in the studies on area shrinkage and recovery,[7] another set of samples was subjected to complete shrinkage and apparent volume shrinkage and recovery were determined.

As regards raw salted skins, hair was removed by shaving with a view to eliminate the interference of hair and the samples were shrunk. Samples after volume recovery were equilibrated with salt (NaCl) before they were dried for shrunken or recovered state measurements. But there was no proper indication of shrinkage behaviour. Hence samples cut out at the raw stage were soaked in water to remove the salt used for curing, the hair was shaved off and the sample dried. Apparent volume measurements were carried out on salt free samples thus obtained.

Table 1

EFFECT OF PRETANNING PROCESSES ON APPARENT VOLUME SHRINKAGE AND RECOVERY

Determination	Stage at which samples are taken				
	Soaking	Liming	Deliming	Pickling	
T_s (°C)	70 (65)	64 (53)	66 (62)	55 (52)	62* (60)*
'Partial' app. vol. shrinkage	Nil (40)	Nil (21)	Nil (47)	55 (37)	40* (53)*
„ area shrinkage					
'Partial' app. vol. recovery	Nil (9)	Nil (30)	Nil (11)	No indication (20)	No recovery (5)*
„ area recovery					
'Complete' app. vol. shrinkage	Nil (59)	Nil (43)	Nil (65)	31 (51)	24* (73)*
„ area shrinkage					
'Complete' app. vol. recovery	Nil (6)	Nil (26)	Nil (13)	No indication (19)	No recovery (2)*
„ area recovery					

Figures in paranthesis relate to T_s, area shrinkage and area recovery values of 7 wet (non-dried) samples

*Values of samples shrunk in pickle medium

Results and discussion

It is seen from Table 1 that the raw, limed and delimed skin samples shrink at almost the same temperature. In the case of area shrinkage measurements, the shrinkage temperature of the limed samples is very much lower than that of the corresponding samples used for apparent volume measurements. This is due to the fact that all the apparent volume measurements were made in the dried and conditioned state, whereas area shrinkage measurements were made in the wet state. The process of drying and conditioning is responsible for the less capacity of the samples to wet when resoaked in water for determining the shrinkage temperature. Lowered capacity to wet decreases the diluent content (water in this case) in the pelt which results in an increase in the shrinkage temperature.[12] In addition, in the case of limed samples, capacity to rewet is further affected by the decreased wetting capacity of dried lime present in the pelt and calcium carbonate formed on the surface while air drying of the limed pelt. Conversion of lime into its carbonate also lowers the pH of limed skin from 12·4 to 9·0. There is thus a rise in the shrinkage temperature of limed samples compared to the wet limed samples.

Forty samples were studied for apparent volume shrinkage measurements both in the case of 'partial' and 'complete' shrinkage, at each stage of pretanning operations. No change in volume was observed in the case of raw, limed and delimed samples due to 'partial' as 'complete' shrinkage or recovery. It was reported earlier[7] that the change in area due to shrinkage is more in the case of raw and delimed samples than in the corresponding limed samples The area re-

covery of limed samples also behaved in a different manner; shrunken limed samples recover more in area when compared to the recovery property of raw or delimed samples.[7]

This shows that simple air drying influences the apparent volume shrinkage properties. Due to drying, there is a collapse of the collagen net work, leading to glueing up of the fibre in the case of raw and delimed samples, however, dried and rewetted samples do not have the same pelty feel. Due to this, there is less space within the pelt and hence the observed change in area due to shrinkage or recovery is made for in thickness. It was reported by Ramanathan *et al.*[6] that rewetted acetone dehydrated pelt shrunk to the extent of 56% in apparent volume. It is known that acetone dehydration does not bring about a collapse of the fibre net work. These findings on apparent volume shrinkage confirm the influence of air drying on the samples. Since apparent volume measurements were made on the dried samples and area shrinkage measurement on wet (nondried) samples, actual measurements of the change in thickness of raw, limed, delimed and pickled samples due to shrinkage are not possible, because the thickness of the sample itself changes due to drying. Hence in order to have a better understanding of the effect of shrinkage on the thickness of the pelt/leather, it is necessary to conduct both area and apparent volume measurements under similar conditions. Since it is difficult to measure the area of dried samples before and/or after shrinkage at the pretanning stage, studies on area and apparent volume shrinkage of wet (nondried) samples may give an insight into the shrinkage phenomenon.

The effect of drying hinders shrinkage and recovery in volume of limed samples. On pickling the delimed skins, the percentage apparent volume shrinkage is considerably increased whether the samples are shrunk in water or pickle medium; the changes in recovery in the pickle or water medium could not be determined due to overlapping of the values. Increase in per cent apparent volume shrinkage of pickled samples compared to that of delimed samples is perhaps due to quick hydration capacity and retention of net work structure while drying. The apparent volume shrinkage is a little less when the samples are shrunk in pickle medium. However, the difference in value is less significant. This might be the result of two oppositely acting factors (i) removal of salt during soaking and (ii) swelling effect of acid due to dilution of salt. These factors are also perhaps responsible for the overlapping values of apparent volume recovery when water or pickle medium is used.

Conclusion

There is no change in the apparent volume due to shrinkage or recovery in raw, limed and delimed samples though it is reported that pelt shrinks to the extent of 56% in the apparent volume.[6] This may be due to the measurements on samples simply air dried whereas the samples in the previous work were acetone dehydrated. The shrinkage temperature of the samples used for apparent volume shrinkage was higher than that of the samples used for area shrinkage

in a given treatment. This is attributed to the reduced wetting capacity of the dried samples which results in less diluent content.[12] Pickling of delimed skins considerably increases the apparent volume shrinkage, but the apparent volume shrinkage is a little less when the samples are shrunk in pickle medium compared to the values obtained using the water as heating medium.

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